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Introductory Chapter: Photocatalysis – Principles, Opportunities, and Applications

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1. Introduction

Photocatalysis is an applicable technology to control the pollutants and contaminations that are released by industrial activity to the nature. The important feature of photocatalysis is that it is possible to replace the high-temperature reactions to eliminate contaminations with reactions that can take place at room temperature, hence, maintain fossil fuel for other purposes. Heterogeneous photocatalysis process implied a material (usually semiconductor) with a certain bandgap that can be activated by light (at certain wavelength). When the semiconductor crystal is subjected to light with a wavelength higher than the bandgap, electrons are normally activated and move from valence band to conduction band creating a positive hole instead, this process is called electron/hole separation. After formation of electron and holes, one of the two following situations might take place: a) recombination between the electron and holes or b) electron and holes reach the surface and activate an organic molecule on the surface of the semiconductor crystal, that is, electrons will participate in reduction process, while the holes participate in oxidation process. Several free radicals were detected as a result of photocatalytic process, notably hydroxyl radicals ($\cdot\text{OH}$) and superoxide anions ($\text{O}_2^{\cdot-}$). The formed radicals are participating in the continuous reactions with the adjacent organic molecules until total minimization. Therefore, the overall process can be summarized in four main steps: (a) adsorption of organic molecule on the surface of the semiconductor crystal, (b) electron/hole formation, (c) reaction between electron and/or holes with the adsorbed molecule, (d) over-reaction might take place, and (e) desorption of the products (**Figure 1**) [1].

According to Scopus®, in the last 10 years (between 2013 and 2022), the researchers in different fields reported their research results in photocatalysis in more than 66,262 papers (**Figure 2**). Out of these papers, 7850 papers reported the findings in the area of air purification. From these papers, only 1258 papers (only 1.8% of the total photocatalysis publications) discussed the utilization of photocatalysis to purify air from short-chain hydrocarbons. These statistics clearly show that the research in the field of air purification from hydrocarbons needs attention to be developed and improved. Hence, more efforts must be performed in this research area because a clean environment is one of the research strategic plans in most countries.

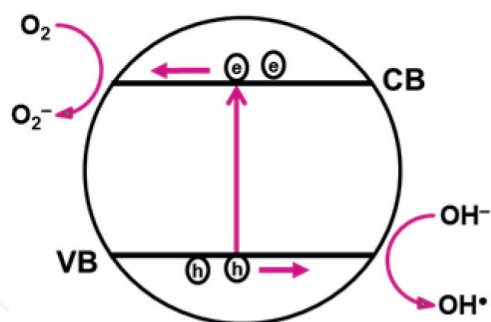


Figure 1.
The photocatalytic process over semiconductor crystals.

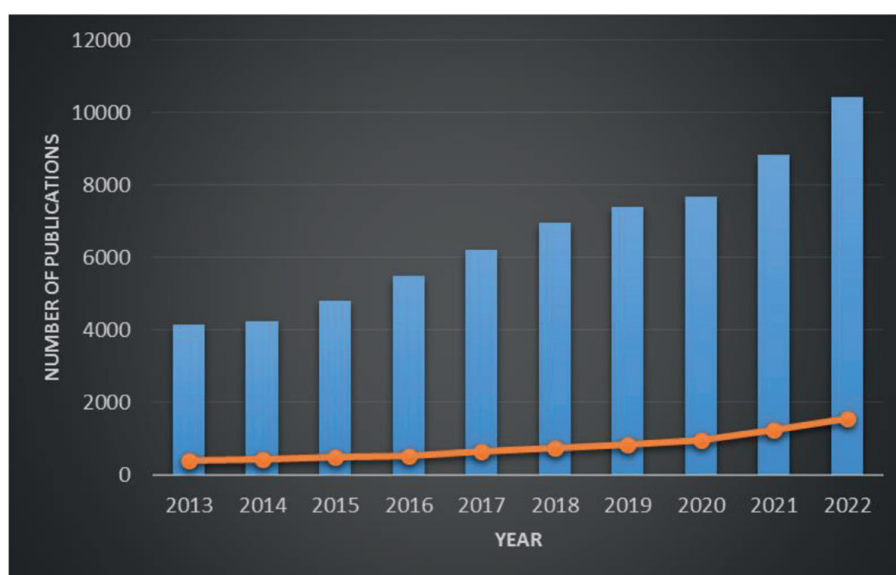


Figure 2.
The number of publications in the last 10 years of the photocatalysis research. The orange line represents the number of photocatalysis in hydrocarbon elimination area.

2. Short-chain hydrocarbons in air

The release of pollutants and contaminants in nature associate with the industrial revolution since the 1800th. Since that, humans were able to release huge amounts of pollutants into air, water, and soil. As the population increases rapidly, the industrial activities have to grow at the same—or even more—rate. As a result, nature is badly affected by releasing such contaminants and severe problems were developing in animals, plants, water, and of course in humans. Few reasons have been identified as main sources of increasing pollutants and contaminations in air, water, and soil. Those reasons include the not-well-planned industrial growth, the continuation of using the old fashion technologies in several simple and manual industries, the presence of huge numbers of small-scale industries with poor facilities, and more importantly, insufficient waste disposal. Scientists realized the fact of fighting/controlling contaminations since 1950s when they realized that contaminations can be a real threat to the nature. Since that, many attempts were reported to control the environmental problems, which have been caused due to the industrial contaminations such as controlling the pollutants in air and in drinking water [2].

The hydrocarbons with a short-chain skeleton, either saturated or unsaturated (also called C1-C3) are representing the threats to the earth. C1-C3 VOC can be released into air from different sources, such as oil plants, during their production and/or in the chemical industries when they are used in them. C1-C3 VOC can be also released as a result of combustion processes, such as waste burning. Moreover, the C1-C3 VOC can also be found in the exhaust fumes of different vehicles, moreover, they can be also found as a result of natural gas combustion in gas power plants. The importance of catalysis for eliminating/reducing human effects on the environment was established several years ago. Generally, almost 95% of the environmental pollution control is carried out by using catalysts. Catalysis considers the major key technology for controlling gas emissions in the different types/scale industries. Catalysis can control gas emissions in two ways, first: by minimizing the number of waste by-products, and second: by treating the gases emitted during the industrial activities. The famous example of automotive catalytic converter is a perfect example of controlling the gas emission by catalysis.

The catalytic reaction of the saturated C1-C3 VOC (e.g. methane, ethane, and propane) is not easy because of the high stability of these compounds. The activation energy needed to oxidize these compounds is high to activate the very stable C-H bonds, while the unsaturated hydrocarbons (e.g. ethylene and propylene) are easy to be oxidized and over oxidized to produce CO₂. Conventional catalysis techniques such as full oxidation by using noble metals (Au, Pt, Rh, or Pd) or the metal oxides of transition elements and doped metal oxides are effective to degrade C1-C3 VOC at elevated temperature (sometimes 800°C). The needed high temperature in addition to the ease poisoning of the catalysts makes the commercialization of such process not feasible because of the extremely high cost of the overall process [3].

3. Semiconductors photocatalysts

Several semiconductors were reported as photocatalysts such as TiO₂, ZnO, CeO₂, ZnSe, ZrO₂, Nb₂O₅, WO₃, SiC, and CdS. The bandgap of each material determine the energy needed from light to be activated, i.e. high bandgap materials need high energy and low wavelength light such as UV, while materials with small bandgap need low energy and higher wavelength light such as visible light. Generally speaking, the photocatalysts should be stable, cost-effective, abundant, non-toxic, active, and operate under different conditions. The photocatalytic process implies the absorption of a photon with a higher energy than the bandgap, hence the electron will be excited from the valence band to the conduction band and electron/hole pairs will be formed. If both reach the surface, electron can participate in reduction reaction and the hole will participate in oxidation reaction. TiO₂ is one of the most interesting materials, and the most studied one in photocatalysis research. This is because TiO₂ is abundant, nontoxic, stable, and very active under UV illumination. However, due to its wide bandgap (3.2 eV), it cannot utilize visible light to be activated. Several attempts have been reported to shift the adsorption band of TiO₂ toward visible light region, such as doping TiO₂ with other metal or metal oxide, creating sub-energy level in TiO₂ lattice, decreasing the crystal size of TiO₂ to nano-level, or forming composite with another material. Several transition elements were reported as dopant for TiO₂, and it showed a shift in the bandgap toward the visible light region such as Cr⁶⁺, V⁵⁺, and Fe³⁺. Moreover, noble metals such as Ag, Au, and Pt were also reported as an electron trap in TiO₂, however, this system is difficult to commercialize due to high cost of

the materials. Creating a sub-energy level also attracts several researchers to increase the activity of TiO_2 in visible light. ZnO is a white powder with a bandgap of 3.2 eV, it has been studied as an active photocatalyst, and it exhibited higher photoactivity in several reactions. Moreover, the degradation of several antibiotic compounds is present in water such as amoxicillin, ampicillin, and cloxacillin. The comparison between ZnO and TiO_2 in the favor of ZnO was discussed. It has been shown that the degradation of cellulose bleaching effluent was investigated by using ZnO and TiO_2 as photocatalysts, ZnO showed better activity than TiO_2 . ZnO , again, showed better activity than TiO_2 in the degradation of Acid Red 14 dye. Furthermore, high activity is also reported for ZnO than TiO_2 (Degussa P25) in the degradation of Acid Brown 14 dye under different operating conditions. WO_3 is a pale yellow semi-conductor metal oxide with a bandgap of 2.8 eV. Here, WO_3 differs from TiO_2 and ZnO in its light adsorption capacity, it absorbs light up to 500 nm, which indeed gives an advantage over TiO_2 and ZnO . Many authors reported the photocatalytic activity of WO_3 with a certain co-catalyst [4].

4. Oxygen-defected semiconductors

The oxygen-defected semiconductors attracted a lot of interest in the last decade. The idea behind the oxygen-defected semiconductors is modifying the semiconductor lattice through the presence of few oxygen vacancies. This can be achieved *via* either synthesis of the semiconductor in limited oxygen environment (two-step synthesis) or extracting some oxygen from the lattice of the semiconductor (two-step synthesis). The high photocatalytic activity of the oxygen-defected semiconductor can be related to the creation of a sub-energy level below the conduction band of the semiconductor. This sub-energy level can be used for electron relaxing after electron/hole pair formation, therefore, this relaxing minimizes the recombination between the photo-generated electrons and holes. In **Figure 3**, the creation of sub-energy level and its role in photocatalysis process is illustrated.

TiO_2 was the first reported semiconductor that can create oxygen-defected sites in the crystals lattice. Mao et al. reported in Science [5] that reduced titania (TiO_{2-x}), which contains oxygen vacancies sites, $\text{V}_\text{O}-\text{Ti}^{3+}$, is much more active under the visible light illumination than the equivalent TiO_2 . Mao used the hydrogenation technique at elevated temperature to reduce the commercially available TiO_2 . Later, it was reported the one-step *in-situ* reduction of TiO_2 by NO and CO as reducing gases to produce blue titania, the produced material showed high photocatalytic performance in water

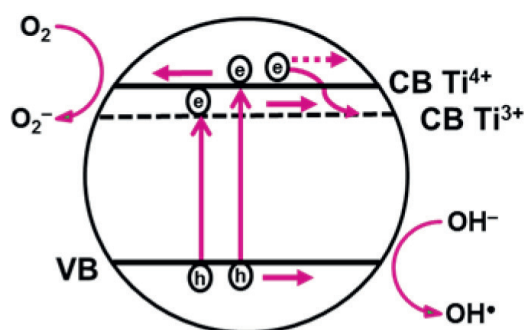


Figure 3. The oxygen-defected TiO_2 and the sub-energy level created as a result of oxygen vacancies.

splitting reaction than neat titania. It has been pointed out that the high activity of the hydrogenated titania in the decomposition of water contaminants (sulfosalicylic acid and phenol) under the illumination of UV. Several reports were published describing different techniques to create Ti^{3+} in TiO_2 such as the thermal treatment under vacuum or poor oxygen environment and thermal treatment at elevated temperature with reducing agents. More complicated methods were also reported such as laser treatment at elevated temperature > 500 K or bombardment with high-energy particles such as neutrons or γ -ray.

Moreover, the oxygen-defected ZnO was synthesized by several techniques such as the reduction of ZnO thin films by biogenic tactic. The photocatalytic performance of the prepared material was evaluated in the degradation of different dyes and 4-nitrophenol, results showed higher degradation rate than neat ZnO, however, stability of the oxygen-defected ZnO was not discussed. Furthermore, it was presented a computational study about the oxygen-defected sites in ZnO. In a third study, it was discussed the synthesis of oxygen-defected ZnO nanorods by thermal treatment for zinc acetate as a precursor, and although the photocatalytic activity was higher than neat ZnO in the degradation of methylene blue dye, stability was not discussed. It is interesting to mention that sometimes oxygen-defected semiconductors can create colored material such as blue titania black ZnO. The synthesis of black ZnO was achieved by hydrogenation technique. Black ZnO showed higher photocatalytic activity than the corresponding ZnO.

Oxygen-defected WO_3 as a photocatalyst was less explored. Only few studies demonstrated the computational calculations about the presence of oxygen-defected WO_3 , stability was not discussed. In a recent report, it has been reported the electronic structure of WO_3 was changed by incorporating different metals, however, the discussion about oxygen-defected and the stability were not discussed.

5. Carbon nitride g- C_3N_4

Graphitic carbon nitride is a very versatile material discovered in 1843 by Berzelius and Liebig [6]. The interesting thing about is that several techniques have been reported for the synthesis of C_3N_4 with a variety of precursors such as the thermal decomposition of melamine. Moreover, it was reported that the synthesis of carbon nitrides can be proceeded through a condensation method with cyanurichloride and calcium cyanamide. In another synthesis procedure, high pressure and high temperature were applied to create carbon nitride from 2-amino-4, 6-dichlorotriazine. In another study, it was reported that the synthesis of carbon nitride can be performed by using cyanurichloride and sodium amide by heating at $200^\circ C$ in benzene. Recently, carbon nitride has attracted the researchers in photocatalysis area because its small bandgap makes it utilize light in visible light areas of the solar spectrum. Hence, the choice of the precursor and the synthesis conditions are extremely important factors to achieve the demanded structure.

One of the famous composites was g- C_3N_4 with TiO_2 . Chang et al. [7] reported a sol-gel technique to create a series of $TiO_2/g-C_3N_4$ composites. The composite showed an excellent liquid phase photocatalytic decolorization of rhodamine B (RhB) dyed solution. $C_3N_4-TiO_2$ composites exhibited 2.4 to 7.0 times higher than solo TiO_2 or N- TiO_2 . Gu et al. [8] reported the synthesis of anatase TiO_2 nano-sheets composite with (g- C_3N_4). The synthesis procedure was the solvent evaporation method. The composite exhibited superior photocatalytic degradation activity of several organic

compounds under the illumination of UV and visible than the parent TiO_2 and C_3N_4 . Zhou et al. [9] reported the synthesis of $g\text{-C}_3\text{N}_4/\text{TiO}_2$ by pyrolysis process of urea and titanium hydroxide. The formed material was evaluated in the gas phase photo-reduction of carbon dioxide and water vapor to form CO and CH_4 . In this paper, the authors confirmed the formation of nitrogen-doped TiO_2 together with $g\text{-C}_3\text{N}_4$ as a separate phase. The photocatalytic behavior of the composite was much higher than the commercial P25. Wang et al. [10] reported the heating of carbon nitride precursor together with TiO_2 ; however, the formed composite was adjacent to particles C_3N_4 and TiO_2 . Although the formed composite was two separate phases, however, the photocatalytic activity was much higher than the parent TiO_2 in H_2 evaluation reaction. Another trial has been reported for the solid state reaction of C_3N_4 precursor and TiO_2 by Boonprakob et al. [11]. The composite of $g\text{-C}_3\text{N}_4/\text{TiO}_2$ was prepared under Ar flow, and the formed sheets were tested in the degradation of methylene blue under visible light. The composite exhibited also higher photocatalytic activity than the parent TiO_2 and C_3N_4 . However, again, the structure formed was adjacent to two separate phases of the mesoporous C_3N_4 and the crystalline TiO_2 . Core-shell structure was not feasible. A third trial was to perform the solid state reaction between the carbon nitride precursor and the pre-synthesized TiO_2 . Although the authors claimed the formation of a thin layer of carbon nitride around the titania particles, but the HR-TEM images they presented did not show such structure, in addition to, and based on our primary experiments, the ratio of C_3N_4 precursor/ TiO_2 , which they presented, cannot lead to a core-shell structure.

6. Porous ceria

Recently, our research group succeeded to fabricate porous ceria with high surface area, almost six times higher than commercial ceria. The interesting thing about the porous ceria is the morphological structure. Commercial ceria has bulky plate-like structure, which is always present in agglomerated form. However, the prepared porous ceria exhibited sponge-like structure with rough surface containing plenty of voids, caves, and channels. This structure was achieved by using citric acid as a fuel in a simple flash combustion method (**Figure 4**) [12].

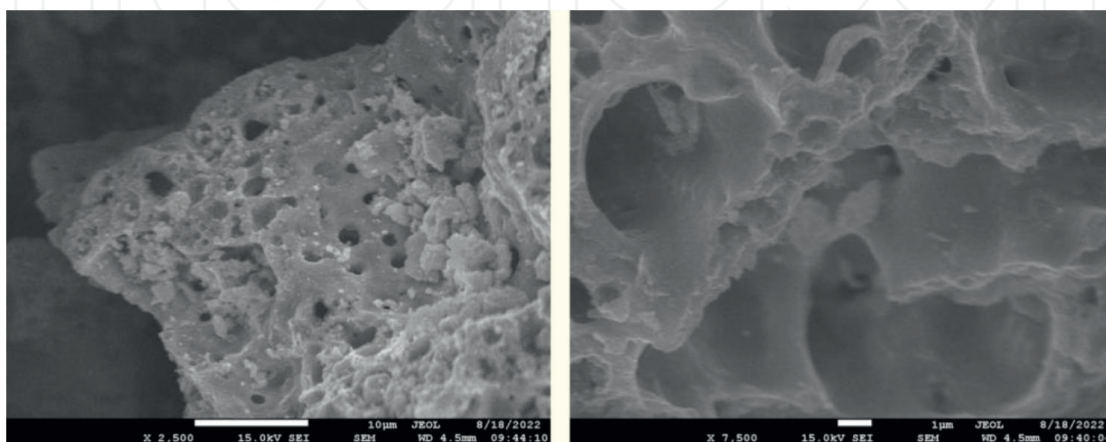


Figure 4.
SEM micrograph of porous ceria.

The prepared porous ceria exhibited high-photocatalytic activity under the illumination of visible light in different applications than commercial ceria. In dye decolorization experiment, methyl green was used as a model compound. It was found that the activity of porous ceria is 3.4 times higher than that of commercial ceria. The second application, the photocatalytic elimination of a gas mixture contains five different short-chain hydrocarbons was applied. Porous ceria was 1.8 times higher than commercial ceria. Currently, our research team is developing the porous ceria by doping with transition elements and the photocatalytic activity is under investigation.

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